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DEVELOPMENTS AND APPROVALS ON TITANIUM, MAGNESIUM AND ALUMINIUM COMPOSITES

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Report Documentation Page

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Presentation outline

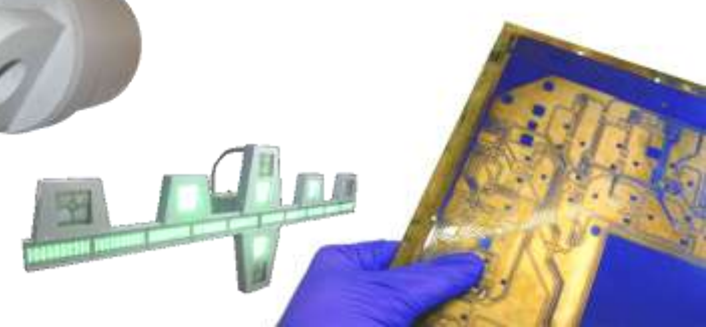
- Introduction to Keronite and our “PEO” technology
- Typical coating characteristics classic applications

Current applications in aerospace and defence:

- Magnesium gearboxes
- Ti6Al4V landing gear bearing carriers

- Al MMC structures

- Other Al applications



Background

Keronite International Ltd. is a Cambridge(UK)-based company that specialises in “plasma electrolytic oxidation”.

This is an electrochemical process for the surface conversion of *any* aluminium or magnesium alloy to give a very hard but compliant ceramic surface.

The process is used for wear protection in many cases where anodising is inadequate. These include applications where superior hardness and wear performance is needed, or where metals such as 2000-series aluminium or magnesium alloys are to be used. It also provides un-rivalled Cr-free corrosion protection for magnesium alloys.

Origins of PEO technology

Applied “PEO” technology has its origins in the former USSR, where it played a role in the longevity of the Mir space station

1986-2001

Courtesy NASA/JPL-Caltech.

Keronite International

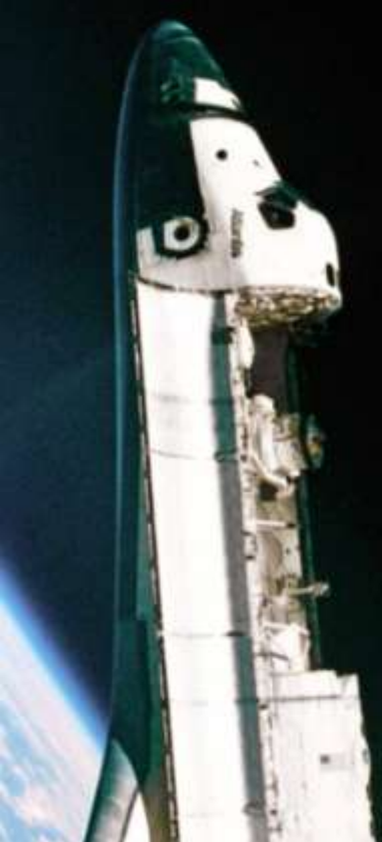
Established in 2000, Keronite specialises in the development and commercial application of **PEO technology** throughout the world

Global HQ in Cambridge (UK)

US HQ in Indianapolis

Partners and licensees worldwide

- Service provider
- Equipment design and installation
- Application engineering
- World leading R&D in PEO



Courtesy NASA/JPL-Caltech.

Business strategy

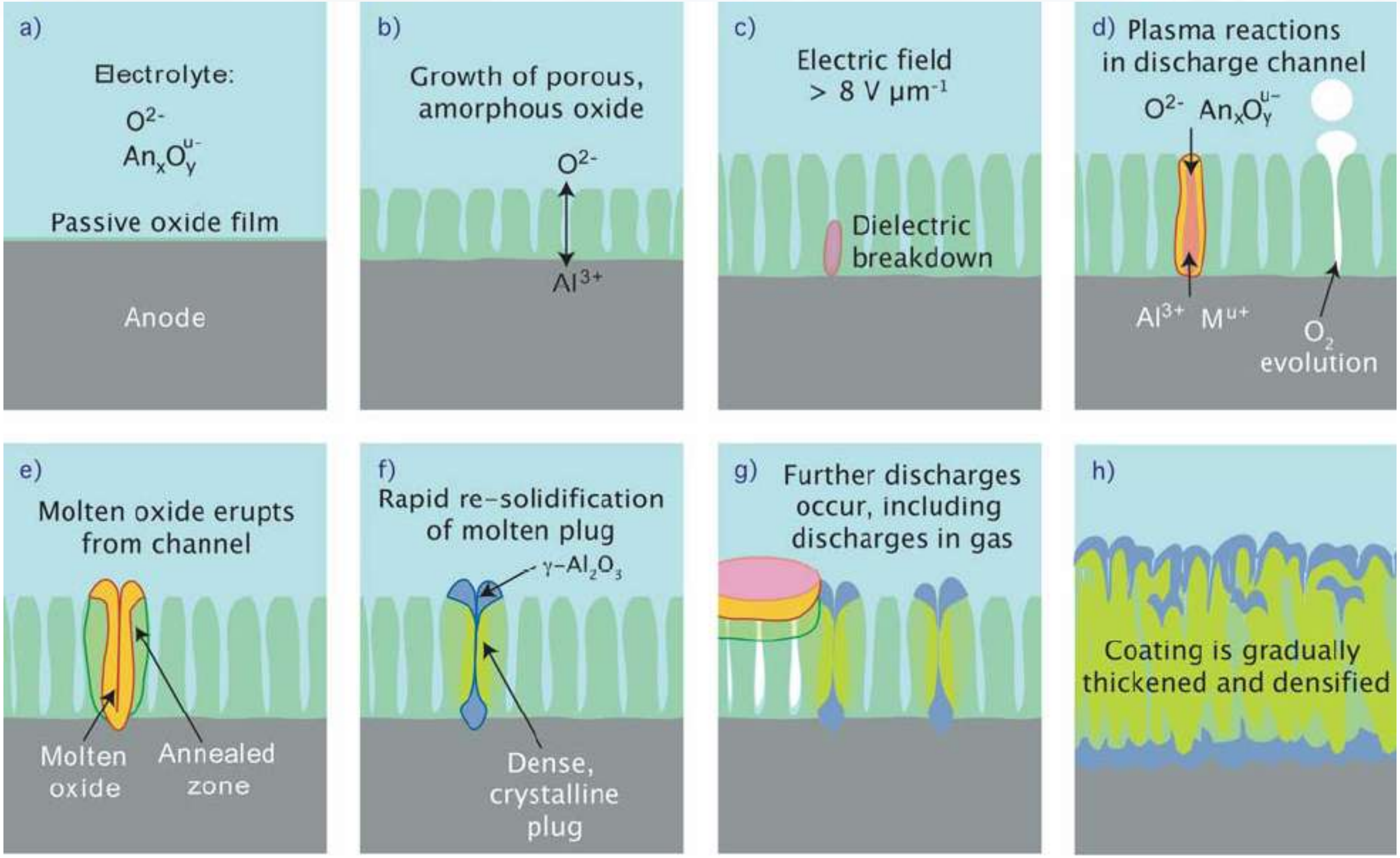
Keronite aims to deliver solutions to our customers in whatever form is most suitable, from R&D and applications engineering, through to small scale production (at Keronite HQ or one of our partners), right up to licensed high-volume production, where we will design, install, and even operate equipment as appropriate

Semi-automated Keronite production line in Korea

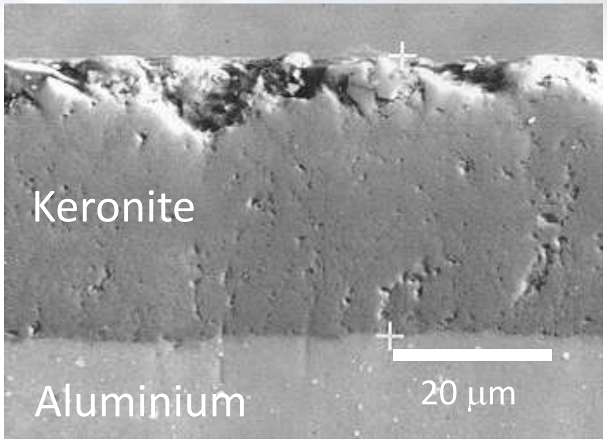
The process in action:

The process is an electrolytic process (like anodising), but employs non-toxic, dilute alkaline electrolytes, and high voltages to generate millions of very short-lived, µm-scale plasma discharges. These melt and modify the growing oxide layer, changing its structure, making it harder, and denser.

Process schematic



Structure & Composition



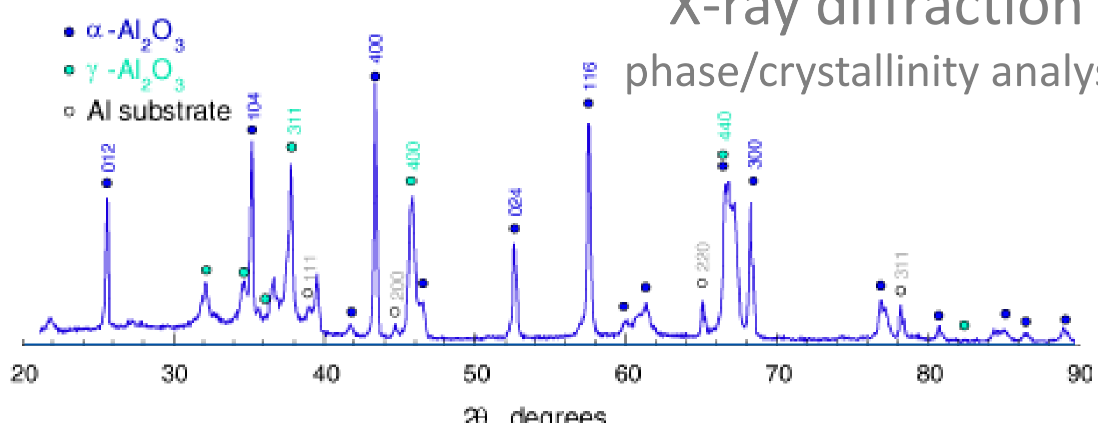
Cross-section

As with anodising, we have a dense, well-adhered ceramic layer, resulting from substrate oxidation. In the PEO process, however, this is modified by melting, melt-flow and re-solidification to become far harder **crystalline phases** such as "sapphire", and also a far more complex microstructure than the simple columnar pores of anodising.

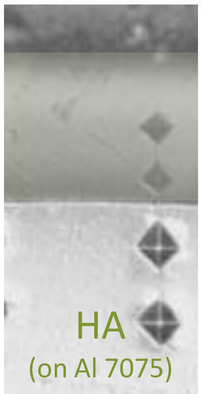
α-Al_2O_3 *corundum*

X-ray diffraction

phase/crystallinity analysis

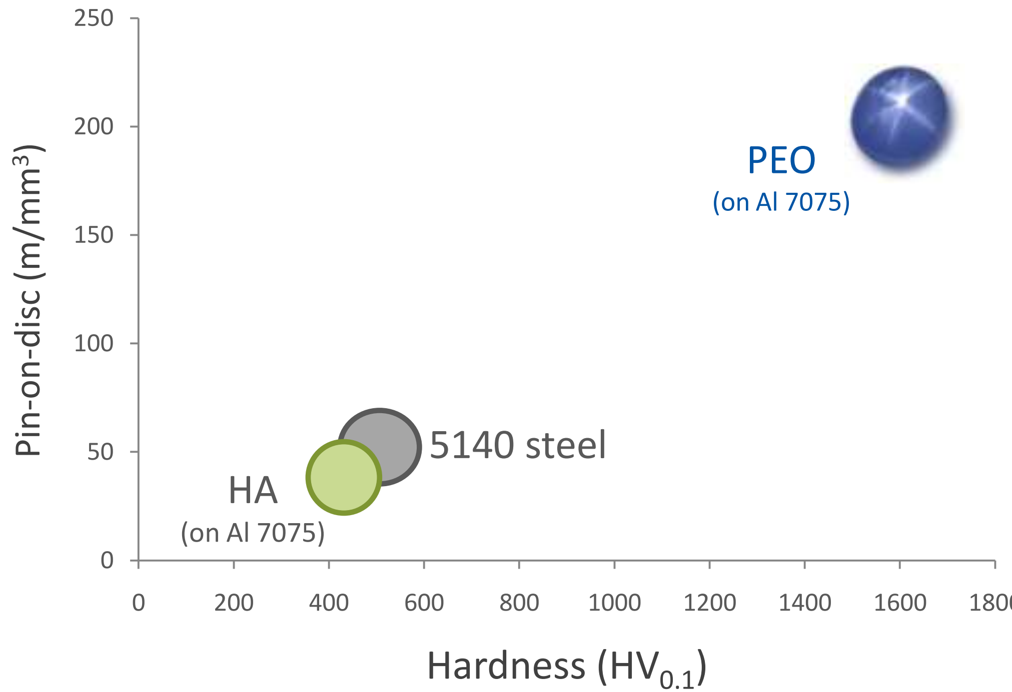


Hardness & wear resistance

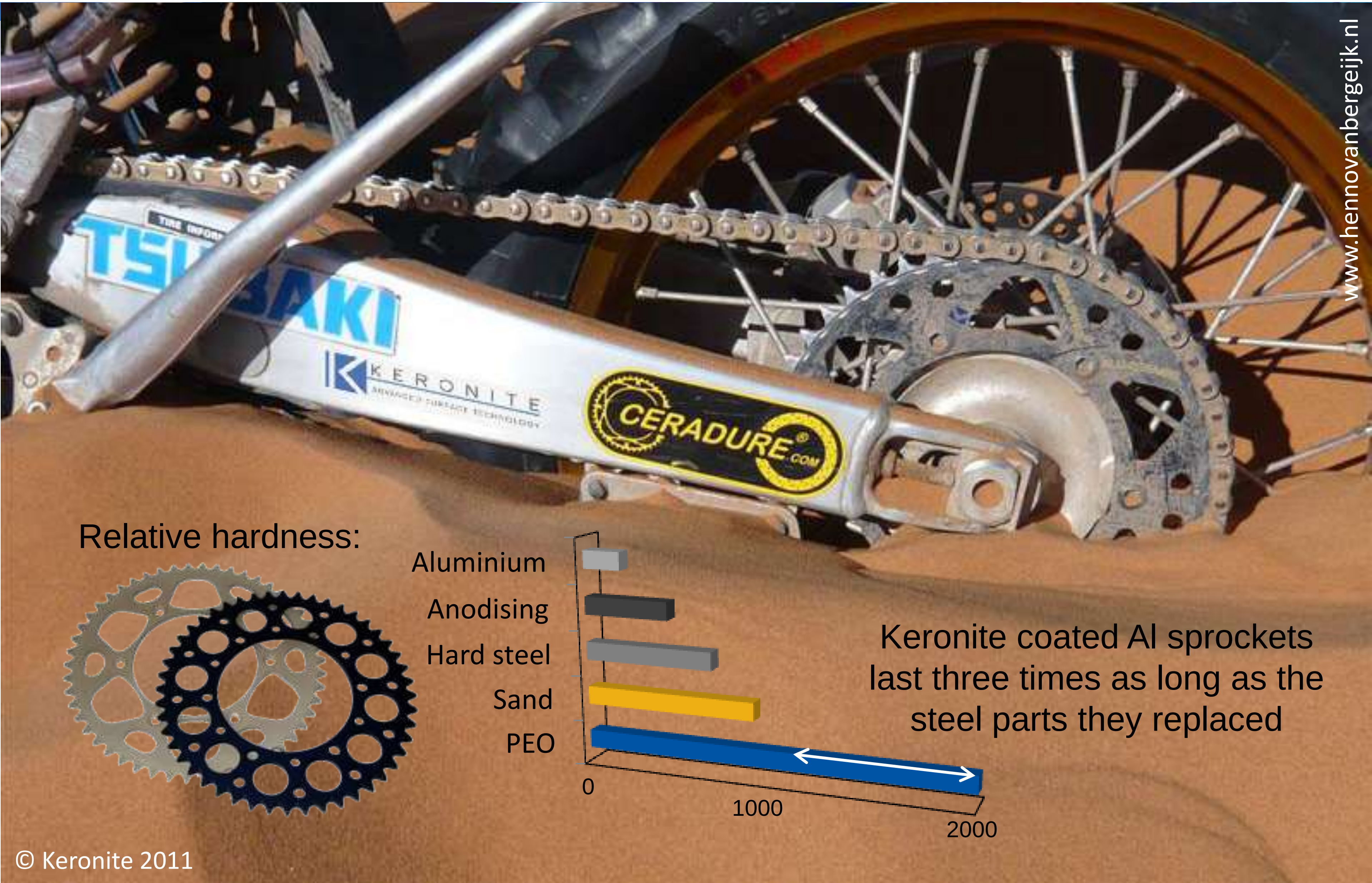


α-Al_2O_3 corundum

The **crystalline phases**, particularly α-Al_2O_3, confer hardnesses of 1500-2000 $HV_{0.1}$ on the Keronite layer, making it significantly harder than steel, sand, glass and many common wear counterparts. This hardness is typically reflected in wear performance:

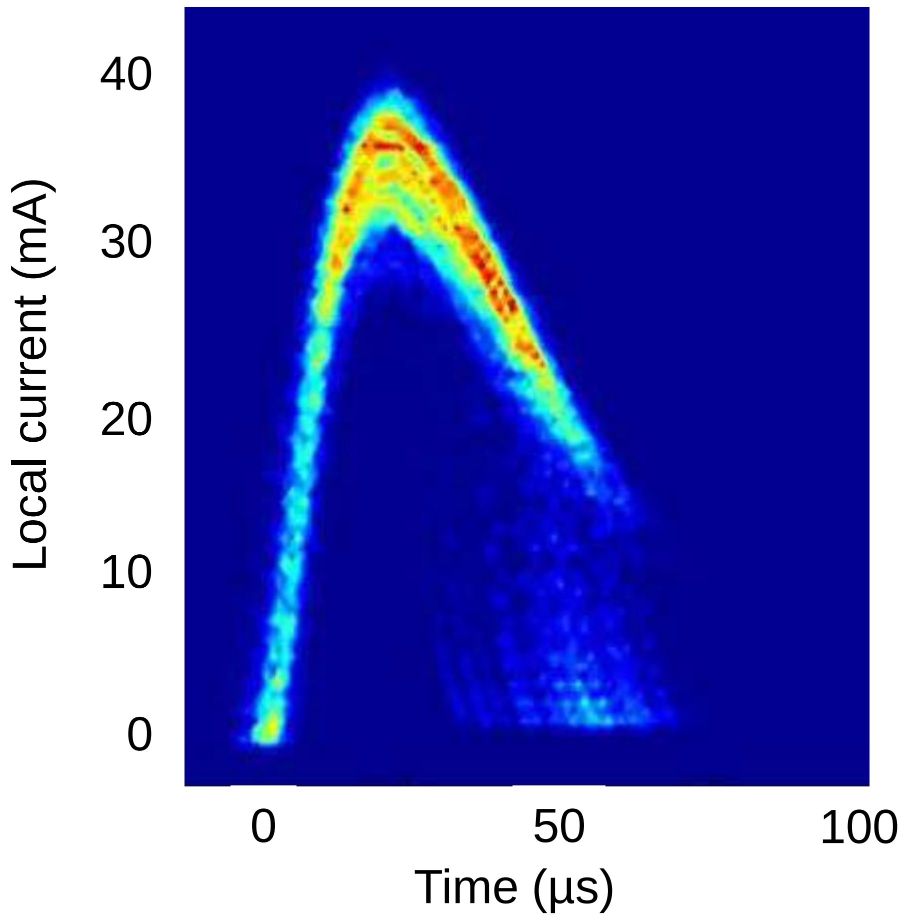


Wear protection



Process control

UNIVERSITY OF CAMBRIDGE



Keronite and research partners in the University of Cambridge possess unique MHz process analysis and control capabilities for characterising individual discharges and plasma parameters such as temperature and composition.

T_{core} = 16000 K

$T_{envelope}$ = 3500 K

Plasma density:

$N_e \sim 10^{15}\ cm^{-3}$

$N_0 \sim 10^{18}\ cm^{-3}$

Characterisation of discharge events during plasma electrolytic oxidation, Dunleavy et al., *Surface and Coatings Technology*, 203 (2009), 22: 3410 - 3419

KERONITE
ADVANCED SURFACE TECHNOLOGY

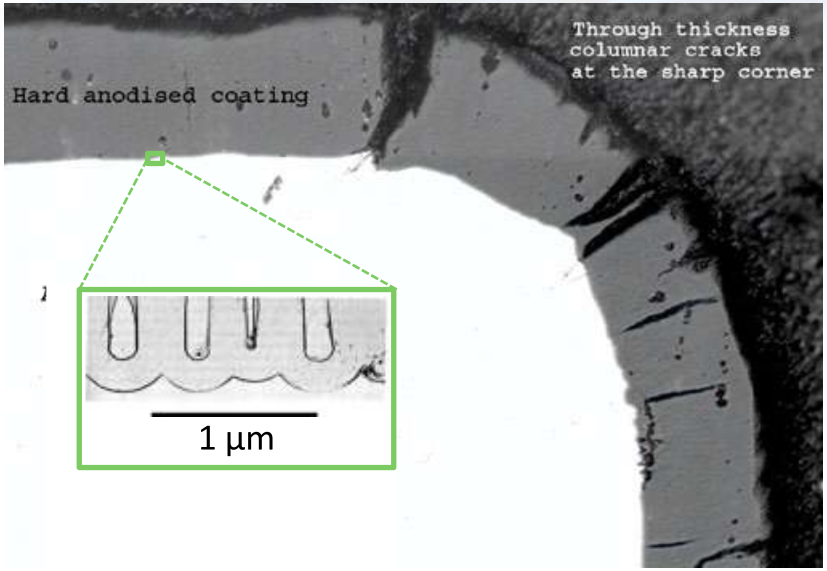
World motorsport

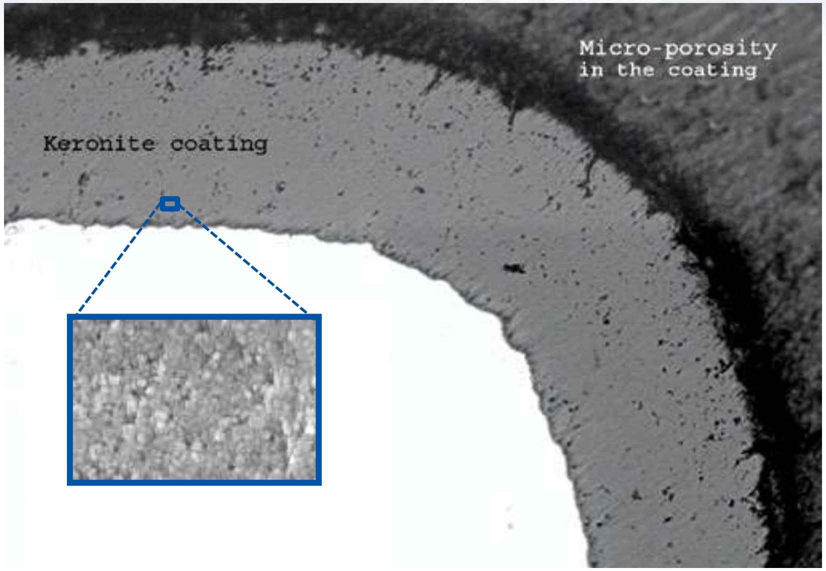
Keronite coatings are widely used in motorsport.

They are in particular demand with many of the worlds’ leading motorsport teams, including F1 teams where Keronite is the most widely applied protective coating for magnesium.

Thermal protection
Magnesium corrosion protection
Hardness and wear protection

Layer structure





Similar to anodising: Uniform coverage of complex shapes
Well-controlled, predictable growth

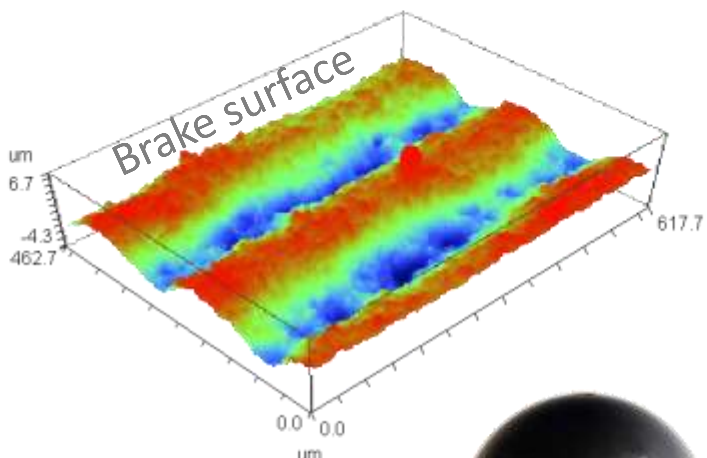
Non-columnar structure: Superior edge protection
Less susceptible to corrosion, wear
Lower fatigue debit

Friction surfaces

The Keronite surface has intrinsic roughness of:

$R_a \approx \frac{1}{10}$ Thickness

This can be enhanced (e.g. profiled substrate) or reduced (e.g. polishing or post-treatment) to give a very wide range of μ



Polished bearing

Approximate examples:

Keronite vs. bearing steel: 0.6-0.7
Keronite vs. Keronite: ~0.6

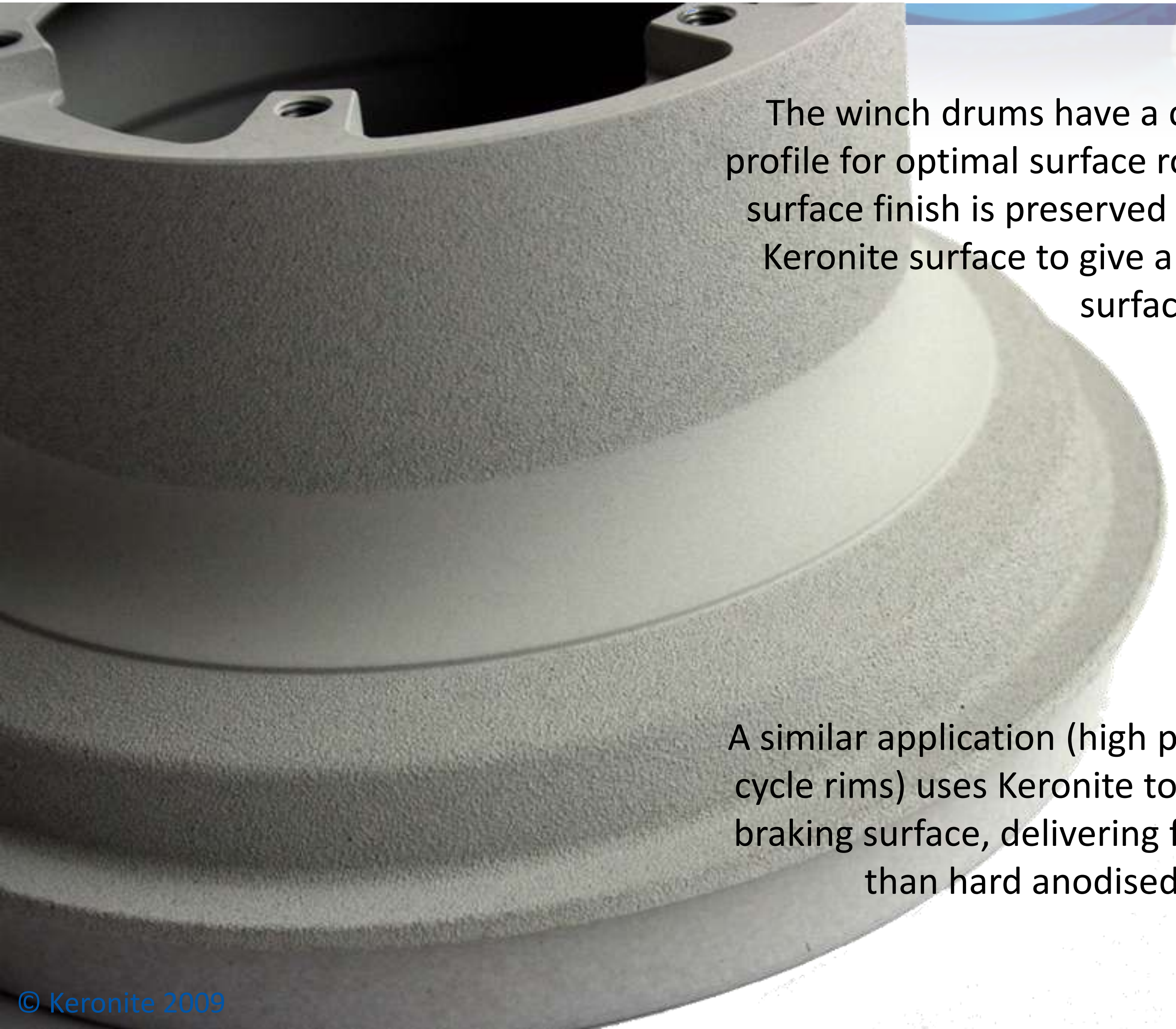
Lubricated Keronite: ~0.1
Polished, lubricated: ~0.03-0.04

Racing yachts (friction)

The America's Cup Yacht *BMW Oracle* pioneered the use of Keronite™ coated winch drums in 2007. These have since been widely adopted in high-performance racing yachts.

Courtesy BMW Oracle

High friction surfaces



The winch drums have a complex shot-peened profile for optimal surface roughness. This complex surface finish is preserved from wear by the hard Keronite surface to give a durable, high-friction surface.

A similar application (high performance off-road cycle rims) uses Keronite to protect a machined braking surface, delivering far greater durability than hard anodised aluminium.

Textured brake surface

Black Keronite provides durable wear protection for a textured braking surface:

Low friction

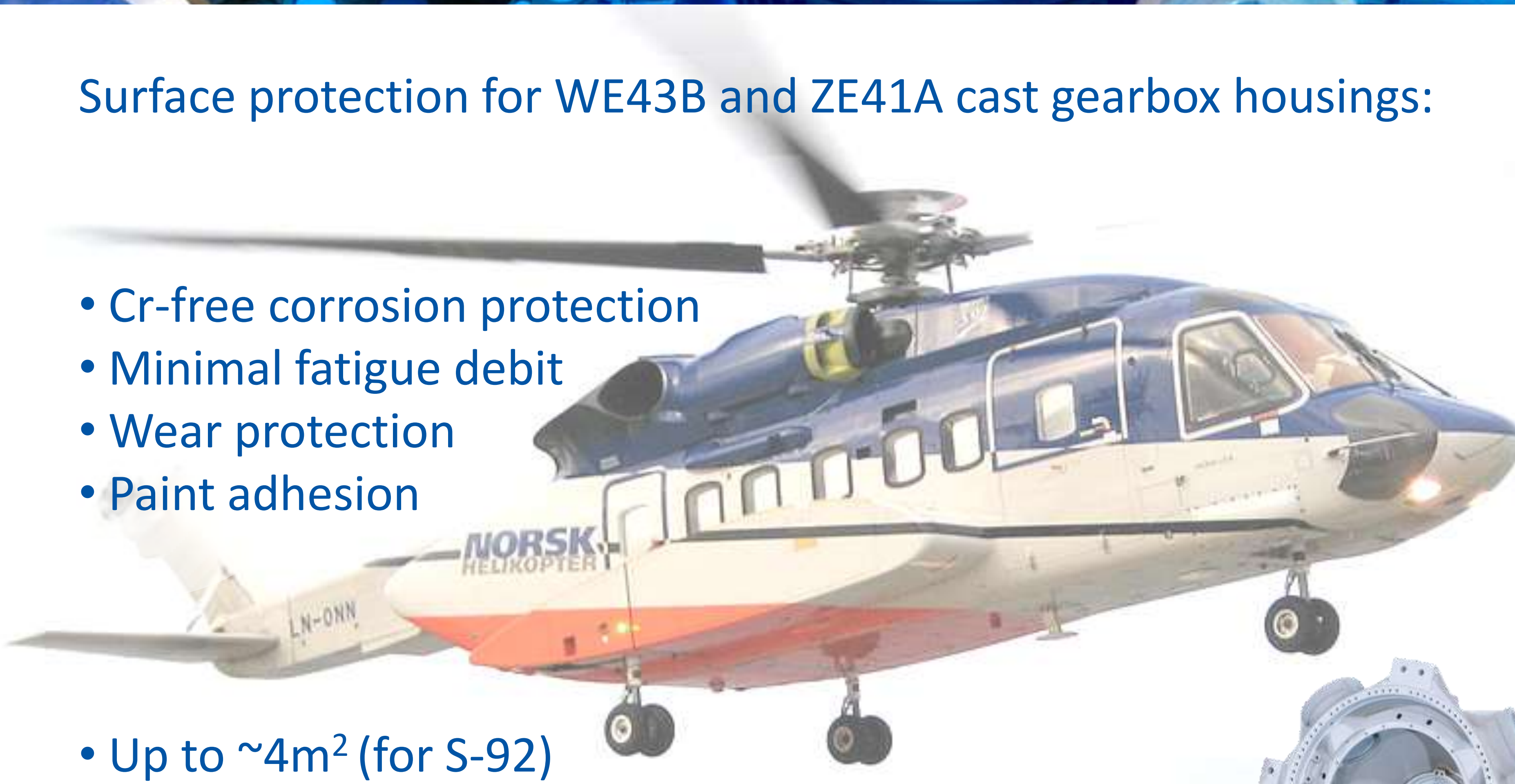
By applying conventional polishing or honing techniques to Keronite surfaces, R_a of just 10s of nm can readily be achieved. This generally amounts to removal of the surface roughness; with the polishing somewhat self-limiting as soon as the bearing area increases.

Polished surfaces retain a very fine pore structure which is ideal for lubricant retention. A honed cylinder liner, for instance, retains lubricant as well as traditional corrugated surfaces, whilst offering far lower friction.

Keronite was an enabling technology for certain aluminium valve-train components in F1 engines when 22,000 rpm was permitted; hard anodising could not provide adequate wear protection.

Mg gearboxes

Surface protection for WE43B and ZE41A cast gearbox housings:



- Cr-free corrosion protection
- Minimal fatigue debit
- Wear protection
- Paint adhesion

- Up to ~$4m^2$ (for S-92)
- DOW17 and HAE replacement (to exceed *AMS 2466*)
- Qualified pre-treatment for Rockhard Resin

Image courtesy of Bristow Norway

Mg corrosion protection

Keronite is the only system to *exceed* the protection offered by Cr(VI) conversion

-Ford Motor Co. research

Magnesium Technology 2005 *Edited by Neale R. Neelameggham, Howard I. Kaplan, and Bob R. Powell*
TMS (The Minerals, Metals & Materials Society), 2005

Evaluation of Corrosion Protection Methods for Magnesium Alloys in Automotive Applications

Blanchard, P.J., Hill, D.J., Bretz, G.T., & McCune, R.C.
Ford Motor Co., Research & Advanced Engineering
2101 Village Road, Dearborn, MI 48121

Keywords: Magnesium, Conversion Coatings, Anodized Coatings and Corrosion

Abstract

Magnesium alloys are susceptible to galvanic corrosion. Consequently, it is often necessary to apply coatings to magnesium components for isolation purposes. However, previous publications suggest the effectiveness of commercial coatings can vary widely. Therefore, an extensive corrosion screening study was performed to evaluate pre-treatment and coating systems currently available for use within the automotive industry. This paper focuses on a selection of conversion and anodized coatings. In many instances, these coatings were used in conjunction with either powder coat or an electro-coat to assess the additional protection offered by a supplemental barrier. Scribe test results and corroded area determination after accelerated corrosion testing are presented and used to quantify the pre-treatment performance. These results are supplemented by DC polarization measurements to determine the level of passivation. Finally, SEM micrographs were used to determine coating thickness variability and morphology. The overall performance of each pre-treatment and coating is then assessed with respect to corrosion protection and robustness.

methods. The sections that follow detail each of the test methods employed and highlight the key observations and suitability of the candidate systems for future implementation.

Material Selection and Experimental Methods

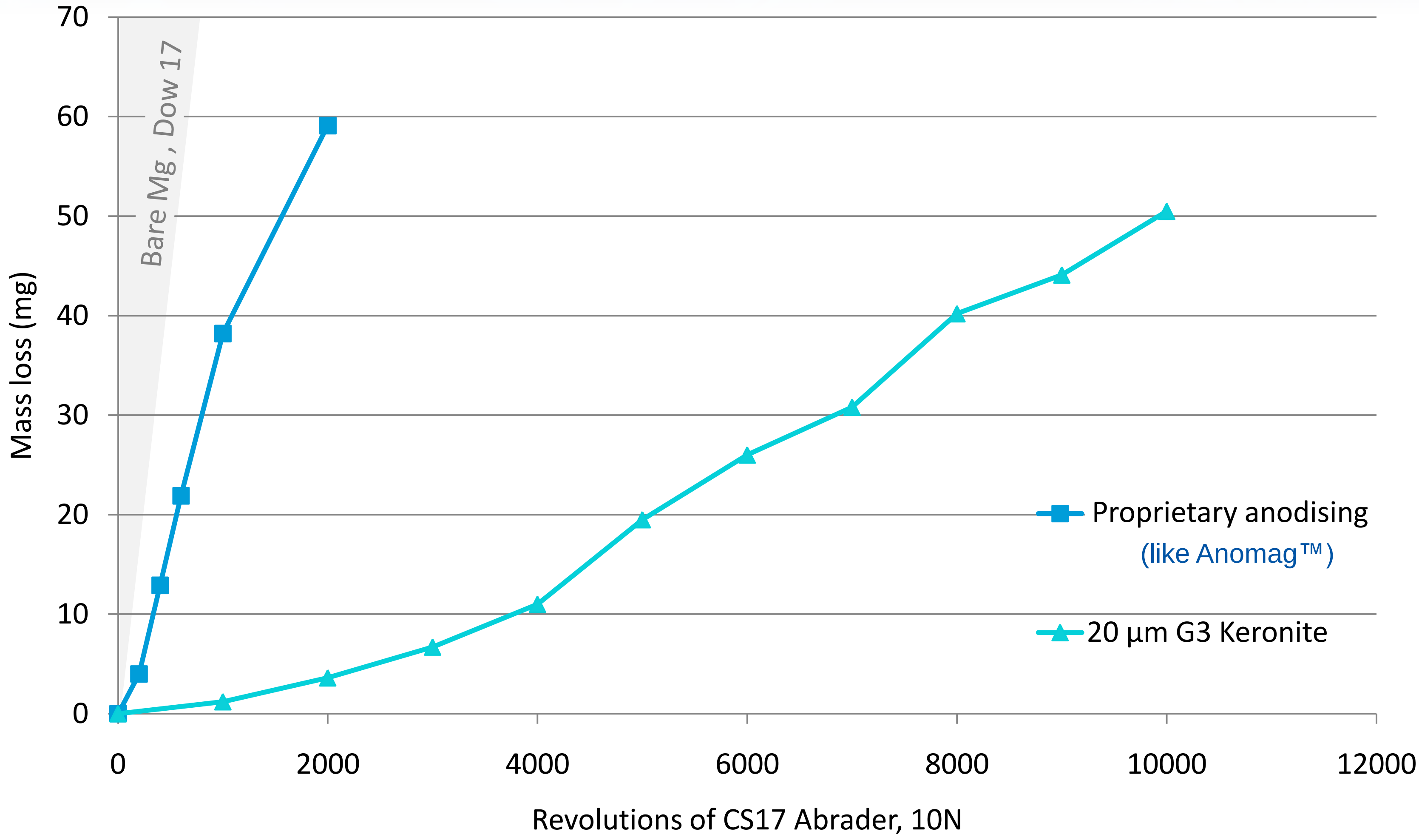
Experimental Test Plan

Table I contains a summary of the coating combinations. In total, seven primary coatings or pre-treatments were evaluated as part of this study. However, since previous studies [2] recommended the use of supplemental barrier layers, in most cases, either an epoxy electro-coat or powder coat was also applied to the primary coating to determine the incremental benefit of these additional layers.

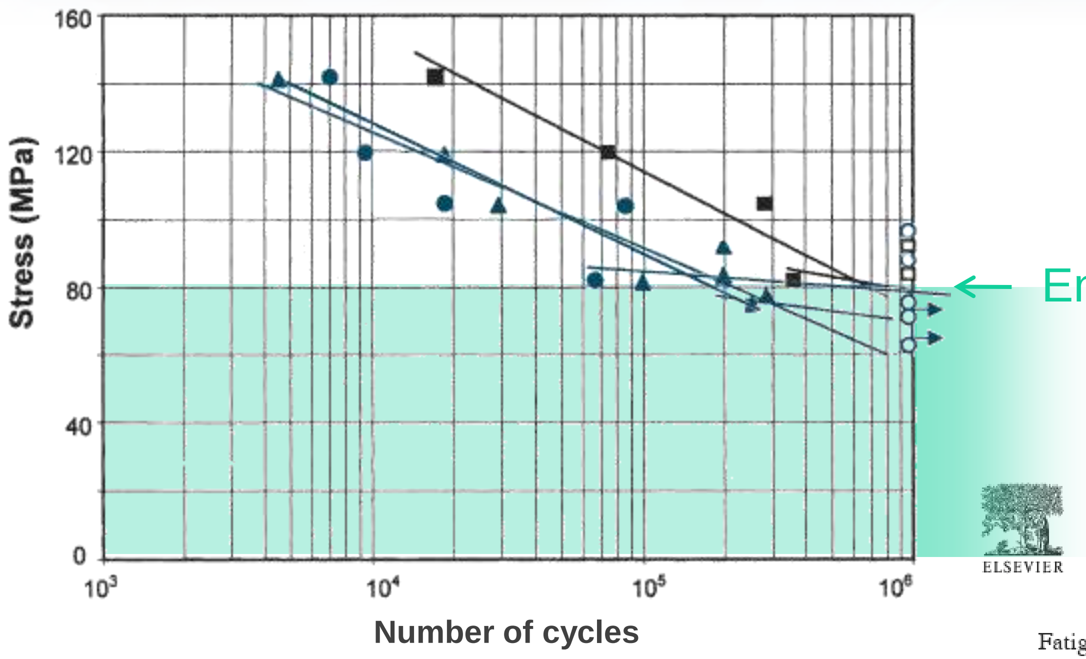
Table I. Sample identification and coating combinations.

I.D.	Primary Coating	Secondary Coating
A	Hexavalent Cr 6 Conversion Coating	Epoxy-Polyester Powder Coat I
B	Cr Free Conversion Coating I	None
BC	Cr Free Conversion Coating I	Epoxy E-Coat II
C	Cr Free Conversion Coating I	Epoxy E-Coat I
D	Cr Free Conversion Coating I	Epoxy-Polyester Powder Coat I
E	Cr Free Conversion Coating I	Organic Sealer
F	Anodized I - 5µm	None
[illegible]	Anodized I - 5µm	Epoxy E-Coat I
[illegible]	[illegible]	Epoxy-Polyester Powder Coat I

Mg Taber abrasion



Fatigue endurance



	Batch	Layer thickness (mm)	Endurance limit (MPa)	Fatigue life (cycles)
■	As received Mg	–	85	6.5×10^5
	1	7	81	2.3×10^5
▲	2	15	77	2.8×10^5
●	3	15	83	1.3×10^5

○ Open symbols signify no failure

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Surface and Coatings Technology 182 (2004) 78–84

SURFACE & COATINGS TECHNOLOGY

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Fatigue properties of Keronite® coatings on a magnesium alloy

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Received 2 April 2003; accepted in revised form 15 July 2003

Abstract

In the paper, the feasibility of using the Keronite® plasma electrolytic oxidation process to overcome the problem of fatigue performance reduction caused by anodising treatments in a Mg alloy is studied. Two types of coatings produced using different current regimes, and having two thicknesses of ~7 and ~15 μm, were tested using a rotating bending fatigue tester. SEM, XRD and optical microscopy techniques were used to evaluate possible fracture mechanisms involved in the initiation and propagation of the fatigue cracks. The results of the investigation demonstrate that Keronite® coatings may cause no more than a 10% reduction in the endurance limit of the Mg alloy, which is substantially lower than the effect from conventional anodising. A probable cause of that reduction seems to be distortion of the metal subsurface layer rather than structural defects introduced by the oxide film.

Ti6Al4V bearing carriers

Ti6Al4V landing gear bearing carriers for civil airliner MROs

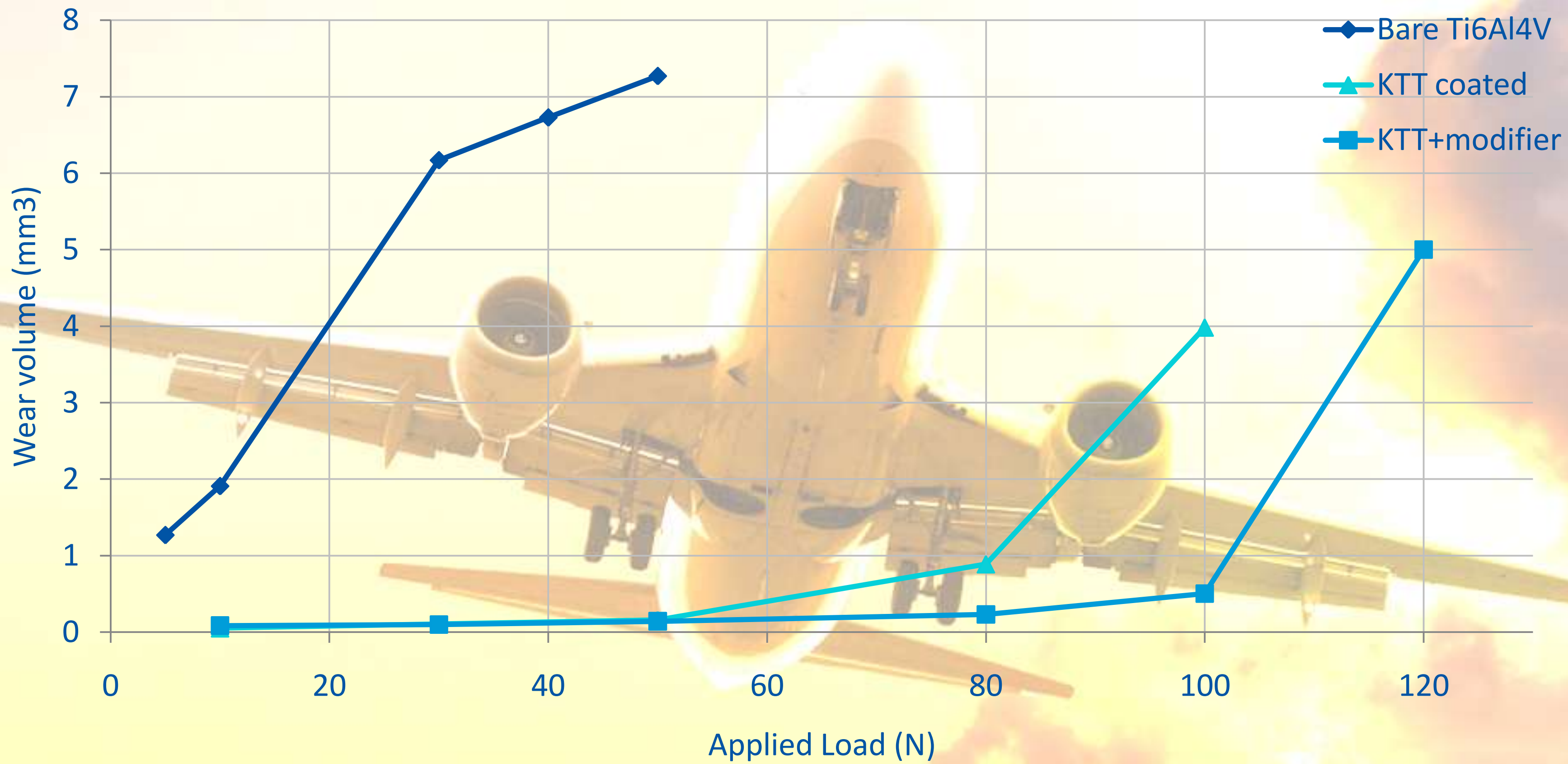
4 parts & 9 bearings per typical airframe

Keronite provides improved bearing refurbishment service:

- Improved wear performance
- Improved anti-galling protection

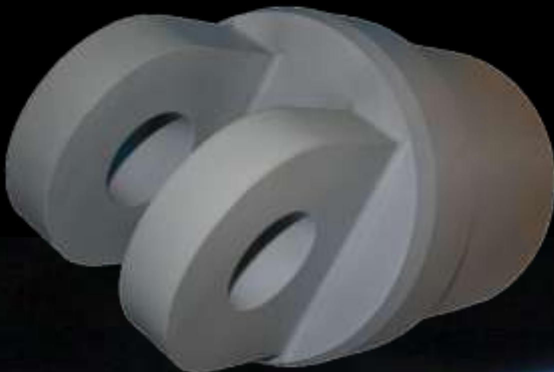
Ti6Al4V wear

Ti6Al4V against SAE52100 steel, block-on-ring dry sliding wear test



PEO layers obtained from mixed aluminate–phosphate baths on Ti–6Al–4V: Dry sliding behaviour, C. Martini et al., Wear 269 (2010) pp. 747–756

Al MMC structures



AMC640xa MMC structural members
AA6061 with 40% SiC reinforcement

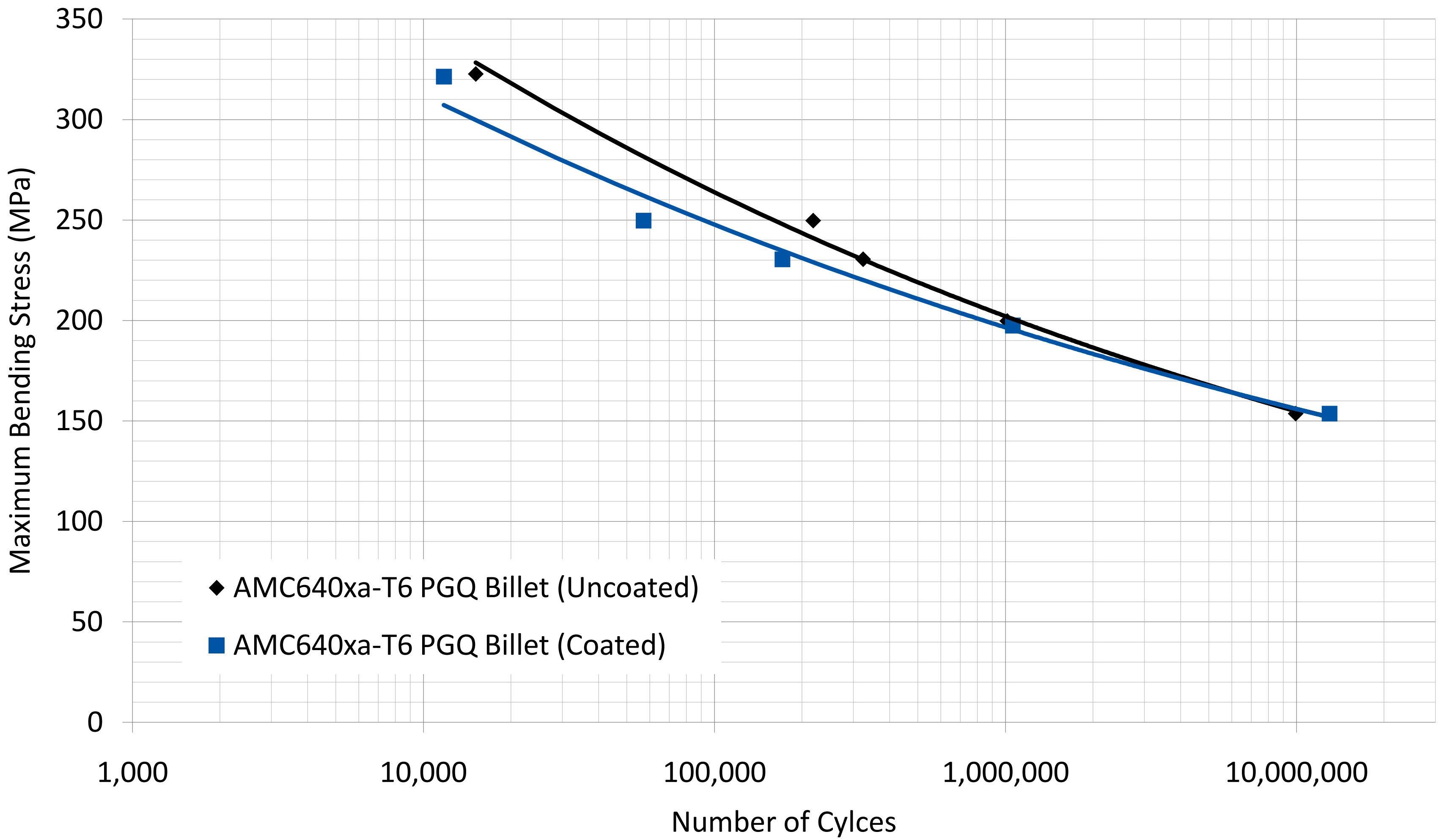
Keronite coated for:

- Corrosion protection
- Fretting wear protection
- Anti-galling protection

… all with minimal fatigue

Image courtesy of NASA

Al MMC fatigue



Fatigue data courtesy of AMC, with permission of ESA

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Thermal stability

Coatings stable to over 900°C (1650°F)

Strain tolerant and resistant to thermal shock and cycles

Moderate thermal conductivities ($k \sim 0.2\text{-}5$ W m^{-1} K^{-1}):

- Thermal protection

  (e.g. Federal Mogul piston crowns)

- Insulating heat sinks

The Thermal Conductivity of Plasma Electrolytic Oxide Coatings on Aluminium and Magnesium
Curran, J.A. and Clyne, T.W., Surface and Coatings Technology, v.199(2-3), pp.177-183 (2005).

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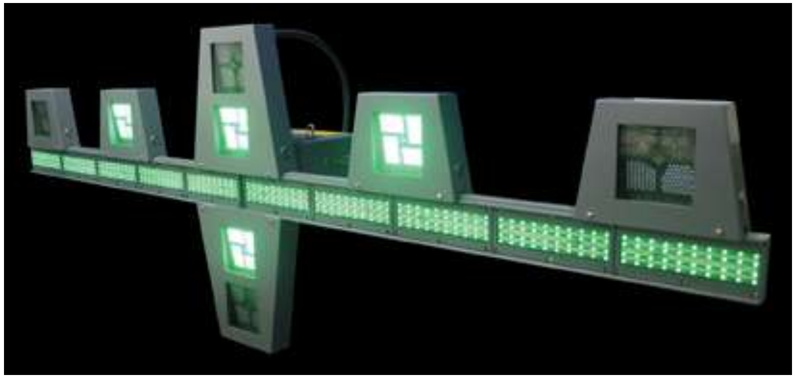
Aeronautical & General Instruments Limited

Naval aviation

Naval aviation lighting systems:

- Paint adhesion
- Corrosion protection
- Thermal barrier function

Naval aviation



Deck and hangar edge lights

HELIVAS approach lights

Stabilised horizon reference systems

High-power substrates

Developed for high dielectric strength (>2kV$_{AC,DC}$) insulation

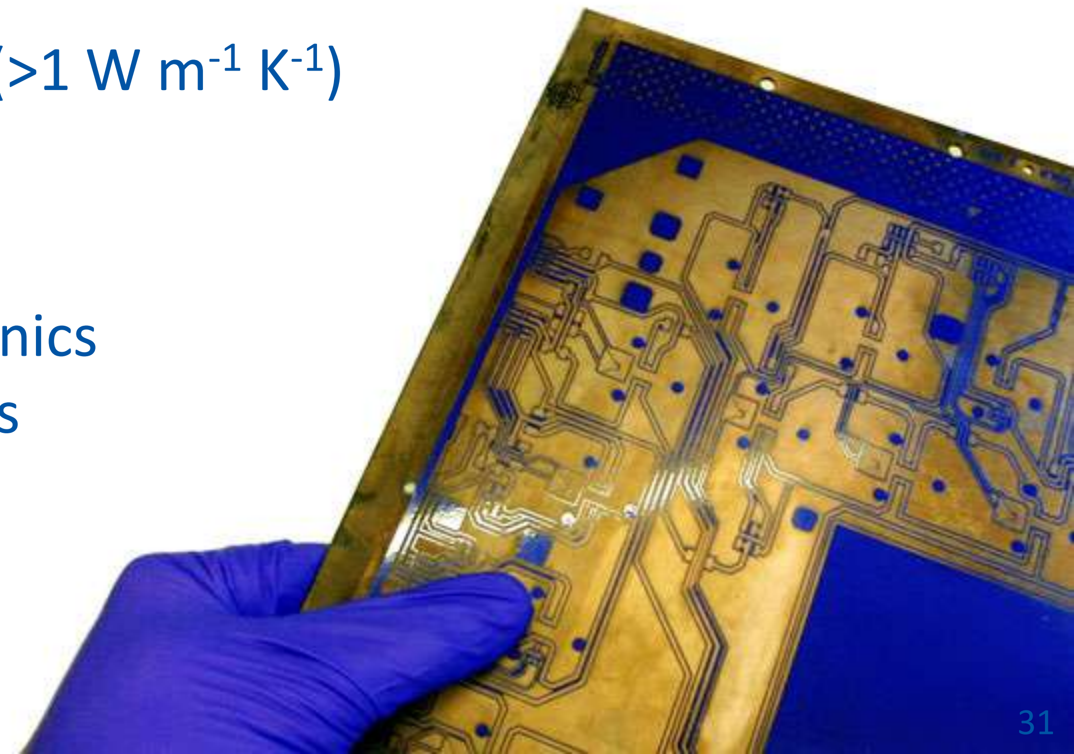
Resistant to thermal shock thermal cycles of over 300°C (570°F)

Coating stable to over 900°C (1650°F)

Minimal thermal barrier (>1 W m^{-1} K^{-1})

Applications:

- High-power electronics
- LED lighting systems
- Plasma processing



Summary

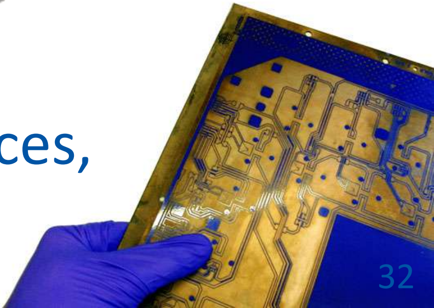
Keronite's surface treatment provides the solution to a wide range of aerospace and defence engineering challenges:

Chrome-free Mg corrosion and wear protection with minimal fatigue debit

Ti6Al4V wear protection

Aluminium wear protection (including MMCs)

Thermal barrier protection, optical surfaces, high power dielectric insulation



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